

## **Electrospun polyaniline/polyethylene oxide nanofiber field effect transistor**

*N.J. Pinto<sup>1</sup>, A.T. Johnson<sup>2</sup>, A.G. MacDiarmid<sup>3</sup>, C.H. Mueller<sup>4</sup>, N. Theofylaktos<sup>5</sup>, D.C. Robinson<sup>5</sup> and F.A. Miranda<sup>5</sup>*

<sup>1</sup>Department of Physics and Electronics, University of Puerto Rico, Humacao, PR 00791

<sup>2</sup>Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, PA 19104

<sup>3</sup>Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104

<sup>4</sup>Analex Corporation, Cleveland, OH 44135

<sup>5</sup>NASA-Glenn Research Center, Cleveland, OH 44135

### **Abstract**

We report on the observation of field effect transistor (FET) behavior in electrospun camphorsulfonic acid doped polyaniline(PANi)/polyethylene oxide(PEO) nanofibers. Saturation channel currents are observed at surprisingly low source/drain voltages. The hole mobility in the depletion regime is  $1.4 \times 10^{-4} \text{ cm}^2/\text{V s}$  while the 1-D charge density (at zero gate bias) is calculated to be approximately 1 hole per 50 two-ring repeat units of polyaniline, consistent with the rather high channel conductivity ( $\sim 10^{-3} \text{ S/cm}$ ). Reducing or eliminating the PEO content in the fiber is expected to enhance device parameters. Electrospinning is thus proposed as a simple method of fabricating 1-D polymer FET's.

Beginning with the initial discovery of conducting polymers three decades ago<sup>1</sup>, intense research in this area has led to all plastic electronic devices<sup>2-5</sup>. Technologically the most important polymer device fabricated and studied is the field effect transistor (FET) as it forms the basic building block in logic circuits and switches for displays. The fabrication (laying down of the active semiconducting channel) of polymer FET's has changed little since their initial discovery<sup>6</sup>. These fabrication techniques include direct electrochemical polymerization of the semiconducting polymer on the electrodes<sup>6</sup>, the use of soluble or precursor materials (spin coating) that undergo subsequent chemical reactions to yield the active semiconducting layer<sup>7-9</sup> and the use of vapor deposition techniques of the semiconducting layer<sup>2,10-11</sup>. The devices thus fabricated have a planar 2-D geometry.

In this paper we present experimental observation of field effect transistor behavior in doped polyaniline/polyethylene oxide (PANi/PEO) nanofibers. We describe a technique called electrospinning to electrostatically lay down the active semiconducting polymer on prepatterned doped Si/SiO<sub>2</sub> substrates, where the oxide thickness was 200 nm. The fundamental difference in this method is that the semiconducting polymer is a nanofiber and so the device has a 1-D geometry similar to devices made from carbon nanotubes<sup>12-13</sup>. Since electrospinning can be used in the controlled assembly of parallel periodic fiber arrays<sup>14</sup> this technology is attractive for fabricating low-cost logic and switching circuits based on conducting polymers.

Although discovered in the 1930's<sup>15</sup> electrospinning is increasingly becoming very popular in the preparation of polymer fibers either in the form of individual fibers or non-woven fiber mats<sup>16-17</sup>. In the present work, 100 mg of emeraldine base PANi was

doped with 129 mg of camphorsulfonic acid (HCSA) and dissolved in 10 ml  $\text{CHCl}_3$  for a period of 6-8 hours. The resulting deep green solution was filtered and 20 mg of PEO having molecular weight 900,000 was added to the solution and stirred for an additional 2 hours. PEO was added to assist in fiber formation. Prior to electrospinning, this solution was filtered using a 0.45  $\mu\text{m}$  PTFE filter to give a homogenous solution. About 1 ml of the solution was placed in hypodermic syringe that was mounted a few degrees below horizontal and the needle connected to 8 kV with the cathode (Al foil) situated about 20 cm from the tip of the needle. Figure 1 shows the basic elements of the electrospinning apparatus. As electric forces on the polymer droplet at the end of the needle overcome the surface tension a jet is issued forth. As the solvent evaporates, fibers of the polymer are seen to collect on the cathode. Individual fibers were collected by passing the patterned Si/SiO<sub>2</sub> wafer in the path of the jet for a few seconds. The fibers were seen to firmly adhere to the substrate. This excellent adherence is largely due to the low surface energy of polyaniline (44 dynes/cm) relative to that of the substrate. However, it is also likely that the nanofibers are highly charged as they impinge on the surface.

Figure 2 shows a scanning electron microscope image of a few electrospun fibers making contact to four gold leads. Only the two fibers contacting the inner leads (source/drain) and labeled *a* and *b* made up the device. The lengths of fibers *a* and *b* were 12  $\mu\text{m}$  and 18  $\mu\text{m}$  respectively while their diameters were 300 nm and 120 nm respectively. The schematic of the device with a fiber is shown in the inset to Figure 2. A Keithley Electrometer model 6517A was used for electrical measurements on the device, which were carried out at 297K in a vacuum desiccator.

The conductivity of individual spun fibers were measured to be  $\sim 10^{-2}$  S/cm. The inset to Figure 3 shows the source drain current ( $I_{S-D}$ ) as a function of source drain voltage ( $V_{S-D}$ ) of the device with no applied back gate voltage ( $V_G$ ). The response is ohmic in the range  $-5 \text{ V} < V_{S-D} < 0 \text{ V}$  as seen (open circles) with no change in the I-V curve upon application of  $V_G$ . When  $V_{S-D}$  was raised to  $-8 \text{ V}$  the current flowing through the fibers increased to  $\sim -50 \text{ nA}$  at which point it started to decrease with time, perhaps due to partial dissociation of HCSA.  $V_{S-D}$  was then turned off and the device left to equilibrate for a few hours. The conductivity of the device decreased to  $\sim 10^{-3}$  S/cm. Subsequent application of  $V_{S-D}$  ( $-1 \text{ V} < V_{S-D} < 0 \text{ V}$ ) resulted in the curve seen in the inset to Figure 3 (closed circles). This curve demonstrates current saturation at  $V_{S-D} < -0.7 \text{ V}$ , and the magnitude of the saturation current was controllable via application of  $V_G$ .

Figure 3 shows the output characteristics of the device for different  $V_G$ . At  $V_G = 0$  V, the I-V curve is linear for low bias voltages with a resistance of  $1.2 \text{ G}\Omega$  and then nears saturation for  $V_{S-D} < -0.7 \text{ V}$ . The source-drain current decreases with increasing  $V_G$  and demonstrates that the device operates as a *field effect transistor* and also that the majority carriers are holes<sup>18</sup> as expected for doped polyaniline<sup>19</sup>. Voltage dependent memory effects in PANi<sup>20</sup> may explain the higher turn-on voltage for  $V_G \neq 0 \text{ V}$ . We assume that the carrier concentration is inherent to the polymer nanofibers and is uniformly distributed along the fiber independent of  $V_G$ . The equation for extracting device parameters in the saturation regime<sup>6</sup> was modified by us to be applicable for nanofibers as

$I_{S-D} = \mu(C_1/L_1^2 + C_2/L_2^2)(V_G - V_{th})^2$ , where  $\mu$  is the hole mobility,  $V_{th}$  represents the threshold necessary to completely deplete the fiber,  $C_i$  and  $L_i$  ( $i = 1, 2$ ) correspond to each fibers' capacitance and length respectively. The fiber capacitance per unit length with

respect to the back gate is  $C/L \sim 2\pi\epsilon\epsilon_0/\ln(2h/r)$ , where  $r$  represents the radius of the fiber,  $h$  and  $\epsilon$  represent the thickness (200 nm) and average dielectric constant ( $\sim 2.5$ ) of the device<sup>21</sup>. A plot of  $I_{S-D}^{1/2}$  versus  $V_G$  after extrapolation to the  $V_G$  axis can be used to obtain  $V_{th}$  (82V). Using the above equations we calculate the hole mobility to be  $1.4 \times 10^4$  cm<sup>2</sup>/V s in the depletion mode. The mobility seems to be low given the high conductivity of the fiber but is similar to earlier reports on conducting polymer based FET's<sup>19,22</sup>. It could also be a result of scattering due to defects or disorder at the fiber/gate-oxide interface due to roughness as the fiber conforms to the topography of the surface<sup>21</sup>. The one-dimensional hole density (at  $V_G=0$ ) can be obtained by calculating the total charge on the fiber as  $Q = CV_{th}$ . We find the density of charge along the fiber  $p = Q/eL \approx 5 \times 10^8$  cm<sup>-1</sup>. Wu et al<sup>23</sup> have estimated that 20 polyaniline chains could fit into a 3 nm porous channel. Since the electrospinning process is expected to lead to preferred alignment of polymer chains along the fiber axis we assume the number of chains scales as the diameter of the fiber. If we take 10 Å as the length for a two-ring repeat unit in PANi we estimate that this density corresponds to about 1 hole per 50 two-ring repeat units (1 hole per two-ring repeat unit ideally corresponds to the fully doped state). The device transconductance  $g_m (= dI_{S-D}/dV_G)$  was calculated to be 0.03 nS at  $V_{S-D} = 1$  V and the on/off ratio was 2. These values most likely are a consequence of the low mobility of charge carriers in the device, and can be improved upon by reducing or eliminating the PEO content in the fiber. A second electrospun device was conditioned under similar conditions in air and also showed FET character albeit a weak one i.e. smaller measured  $I_{S-D}$  with reduced signal to noise.

In summary, we present the first experimental observation of field effect transistor behavior in PANi/PEO nanofibers. Saturation currents are observed in the electrospun devices at surprisingly low  $V_{S-D}$ . The device parameters calculated using doped PANi/PEO as the active semiconducting layer have the potential of being improved upon by reducing or eliminating PEO from the fiber thereby decreasing the nonconducting barriers to charge transport between polyaniline chains, which could lead to higher mobility. Finally, the fact that these devices were fabricated using a simple electrospinning technique expands the potential for fabrication of low-cost FET circuits based on organic polymer nanofibers.

This work was supported in part by NSF DMR 0098603 and NASA Grant NCC3-1066. The authors thank Nicholas Varaljay and Keith Johnson (GRC) for the prepatterned substrates.

## Figure Captions

FIG. 1. Schematic showing the main components of an electrospinning apparatus.

FIG. 2. Scanning Electron Microscope image of electrospun PANi/PEO fibers over a prepatterned Si/SiO<sub>2</sub> substrate. Only fibers **a** and **b** contacting the two inner electrodes make up the device. Inset: Schematic cross section of the device showing a fiber bridging the gap between the source and drain gold (Au) electrodes.

FIG. 3. The current voltage characteristics of the FET device made up of two nanofibers (length 12  $\mu\text{m}$  and 18  $\mu\text{m}$  microns and diameters 300 nm and 120 nm respectively bridging the source-drain contacts) at different back gate voltages showing the accumulation and depletion modes. Inset: The current voltage characteristics of the device with no applied back gate voltage. ( $\circ$ ) Ohmic behavior, *does not* change with back gate voltage, ( $\bullet$ ) Saturation behavior, *does* change with back gate voltage.

## References

- <sup>1</sup>C.K. Chiang, C.R. Fincher Jr., Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, S.C. Gau and A.G. MacDiarmid, *Phys. Rev. Lett.* **39**, 1098 (1977).
- <sup>2</sup>F. Garnier, R. Hajlaoui, A. Yassar and P. Srivastava. *Science*, **265**, 1684 (1994).
- <sup>3</sup>G.H. Gelinck, T.C.T. Geuns and D.M. de Leeuw, *Appl. Phys. Lett.* **77**, 1487, (2000).
- <sup>4</sup>H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, M. Inbasekaran, W. Wu and E. P. Woo, *Science*, **290**, 2123 (2000).
- <sup>5</sup>M. Halik, H. Klauk, U. Zschieschang, T. Kriem, G. Schmid and W. Radik, *Appl. Phys. Lett.* **81**, 289 (2002).
- <sup>6</sup>A. Tsumura, H. Koezuka and T. Ando, *Appl. Phys. Lett.* **49**, 1210 (1986).
- <sup>7</sup>H. Fuchigami, A. Tsumura and H. Koezuka, *Appl. Phys. Lett.* **63**, 1372 (1993).
- <sup>8</sup>A.R. Brown, A. Pomp, C.M. Hart and D.M. de Leeuw, *Science* **270**, 972 (1995).
- <sup>9</sup>J.H. Burroughes, C.A. Jones and R.H. Friend, *Nature (London)* **335**, 137 (1998).
- <sup>10</sup>A. Dodabalapur, L. Torsi and H.E. Katz, *Science* **268**, 207 (1995).
- <sup>11</sup>J. Zaumseil, T. Someya, Z. Bao, Y.L. Loo, R. Cirelli and J.A. Rogers, *Appl. Phys. Lett.* **82**, 793 (2003).
- <sup>12</sup>S.J. Tans, A.R. Verschueren and C. Dekker, *Nature* **393**, 49 (1998).
- <sup>13</sup>M. Radosavljevic, M. Freitag, K.V. Thadani and A.T. Johnson, *Nanoletters* **2**, 761 (2002).
- <sup>14</sup>E. Zussman, A. Theron and A.L. Yarin, *Appl. Phys. Lett.* **82**, 973 (2003).
- <sup>15</sup>A. Formhals, US patent No. 1,975,504 (1934).
- <sup>16</sup>D.H. Reneker and I. Chun, *Nanotechnology* **7**, 216 (1996).

- <sup>17</sup>I.D. Norris, M.M. Shaker, F.K. Ko and A.G. MacDiarmid, *Synth. Metals* **114**, 109 (2000).
- <sup>18</sup>S.M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981).
- <sup>19</sup>C.T. Kuo and W.H. Chiou, *Synth. Metals* **88**, 23 (1997).
- <sup>20</sup>B. Villeret and M. Nechtschien, *Phys. Rev. Lett.* **63**, 1285 (1989).
- <sup>21</sup>R. Martel, T. Schmidt, H.R. Shea, T. Hertel and Ph. Avouris, *Appl. Phys. Lett.* **73**, 2447 (1998).
- <sup>22</sup>J.G. Park, G.T. Kim, V. Krstic, S.H. Lee, B. Kim, S. Roth, M. Burghard and Y.W. Park, *Synth. Metals* **119**, 469 (2001).
- <sup>23</sup>C.G. Wu and T. Bien, *Science* **264**, 1757 (1994).





